Allelix INC

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March 30, 1984

Dr. V. Sammugasunderam
Scientific Authority
Dept. of Energy, Mines and Resources
CANMET, Mineral Sciences Laboratory
555 Booth Street
Ottawa, Ontario
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Dear Dr. Shan:

Re: DSS File No. 26SQ-23440-3-9139
Contract Serial No. OSQ83-00199
Title: Bioadsorption of Heavy Metals
From Mineral Processing Streams

In completion of the requirements of the above contract, we submit 10 copies of the final report which comprises of Milestone I and II reports.

In Milestone I, we identified the process of recovering uranium using fungal mycelium as the bioadsorbent as the most developed model for designing a pilot-scale process for the recovery of heavy metals from mineral processing streams. This was based on our evaluation of the literature for the state-of-art of bioadsorption technology in mining applications.

For Milestone II, we proposed a process schematic for designing the most feasible pilot plant process based on the available bench scale data on the adsorption of uranium by fungal mycelium. We identified as the most appropriate design, a filter press system which involves clamping fungal mycelium in a series of three filter presses and flowing the feed solution through them at a rate of 4 L/min. A good alternate system design is also included.

... 2

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In conclusion, we recommend that this Program proceed to Phase II in which a pilot plant can be constructed based on our proposed schematics.

We are confident that you will agree with our proposal and look forward to your response.

Yours truly,

ALLELIX INC.

Graham Strachan
Vice President and
Commercial Director

Rose Eng Wong
Project Co-ordinator

GS/REW/ms

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BIOADSORPTION DES MÉTAUX LOURDS LORS DU TRAITEMENT MINÉRAL LIQUIDE

PHASE I

RÉSUMÉ

Ce travail a été fait sous les auspices du au centre canadien de la technologie des minéraux et de l'energie, Energie, Mines et Resources, Canada.

DSS NUMÉRO DE DOSSIER : 26SQ.23440-3-9139
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BIOADSORPTION DES MÉTAUX LOURDS LORS DU TRAITEMENT MINÉRAL LIQUIDE

PHASE I

RÉSUMÉ

1 ère étape

Evaluer et analyser la documentation publiée sur les procédés de bioadsorption pour la récupération de métaux lourds dans l'industrie minière et identifier l'un de ces procédés sufisamment documenté qui permettrait l'implantation d'un laboratoire pilote.

2 ièmè étape

Concevoir un procédé schématique pour un laboratoire pilote, basé sur le procédé identifié précédemment dans l'étape I.

Stratégie

La classification suivante a été adoptée pour les procédés candidats selon la nature du biosorbent:

1. Boue activée (cultures microbiennes mixtes)
2. Cultures bactériennes définies
3. Levures et Champignons (moisissures)
4. Algues
5. Dérivé microbien (cellules immobilisées, exopolymères)

Les informations disponible sur chacun de ces cinq sujets ont été analysés d'un point de vue technique et économique. Le but ultime de ce programme est de développer un procédé(s) bénéfique(s) à l'industrie minière canadienne. La considération première de cette étude est avant tout l'aspect technique mais les facteurs économiques et pratiques de chacun de ces procédés yont été traités.

Le critère clé pour la réussite d'un de ces procédés est la valeur par cout unitaire de biomasse du métal recouvré. Cette évaluation économique est basée sur plusieurs facteurs. Ces facteurs sont: la disponibilité et le cout du biosorbent, la possibilité de régénérer et de réutiliser la biomasse, l'efficacité de l'adsorption des solutions provenant des opérations minières à des températures critiques et la valeur du ou des métaux recouvrés.

Plusieurs facteurs influencent la bioadsorption des métaux lourds par la biomasse microbienne, les facteurs sont: les caractéristiques du microorganisme, la nature du métal, les conditions de croissance et l'age de la culture, le pH et la température, la concentration du métal et autres cations et anions ainsi que la presence de résidues organiques

(toxiques pour les cellules) suite aux procédures d'extractions. Tous ces facteurs auront un effet important sur le procédé choisi ainsi que sur l'opération meme.

Discussion des résultats

Il y a deux méchanismes connus d'incorporation qui se produisent chez les microorganismes. La bioadsorption, l'incorporation passive physico-chimique des métaux lourds provenant de diverses solutions est considéré de loin comme étant le procédé le plus adéquat. L'incorporation est généralement rapide, le métal est recouvré ce qui permet la réutilisation du biosorbent. Par contre, la bioaccumulation, l'accumulation intracellulaire active du métal par un microorganisme pouvant le métaboliser, est limitatif d'un point de vue économique puisque le métal ne peut-être récupéré sans la destruction du biosorbent.

Notre estimation de la documentation publiée, révèle qu' il y a des insuffisances dans les données, ceci pouvant avoir un impact sur la possibilité de réalisation du procédé choisie.

1. Les biosorbents n'ont pas été évalués adéquatement avec des solutions tests ressemblant au traitement mineral liquide actuel.

2. A l'exception de l'uranium, les données sur la régénération des métaux lourds couplés aux biosorbents ne sont pas bien documenteés.

3. L'approvisionnement ou la production de quantité suffisante de biomasse ainsi que les besoins nutritifs des microorganisms n'ont pas été étudié.

4. Il n' y a aucune données publié sur les calculs de l'equilibre de la biomasse ou sur le traitement schématique.

Cependant nous pensons que le traitement peut-etre développé en se basant sur les données disponible moyennant certaines études périphériques.

Nous proposons que le procédé candidat soit classé selon le métal à récupérer. L'uranium est le meilleur élément cible pour ce type de traitement peusqu' il démontre une bonne bioadsorption ainsi qu' un bon rendement quant à la régénération du biosorbent.

Nous avons classé les différents biosorbents pour la récupération de l'uranium selon 5 catégories.

1. Mycelium de Champignons (moisissures)
2. Dérivés microbiens (Cellules immobilisées, exopolymères)
3. Cultures microbiennes mixtes (Boues activées)
4. Levures ou Cultures bacteriennes définies
5. Algues

Certaines espèces de Champignons/Moisissures ont démontré un haut niveau d'incorporation de l'uranium(VI) en solution aqueuse. L'uranium peut-etre récupéré, en lavant la biomasse chargé du métal, avec une solution de sels de carbonate (Ex: 0.1 M carbonate de sodium). Ces deux qualités sont très rechercées lors du procédé de bioadsorption.

Certains facteurs, cependant, restent à confirmer soit: l'adsorption de la biomasse pour l'uranium en présence de fortes concentrations d'anions et de cations (caractéristique au traitement minéral liquide), les caractéristiques physiques du biosorbent et par conséquent ses propriétés de manipulation, la viabilité à long-terme du biosorbent et finalement les démarches économiques inhérente à la production du biosorbent. Ces

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facteurs varieront selon l'espèce de Champignon/Mosissure choisie, sa disponibilité et sa source (ex: un sous-produit de la fermentation industrielle).

Les autres procédés candidats ne sont pas aussi bien développés quant à la récupération des métaux lourds autre que l'uranium, nous avons classé les biosorbents comme suit:

1. Cultures Bactériennes définies
2. Cultures Microbiennes mixtes
3. Dérivés microbiens (cellules immobilisées, exopolymères)
4. Champignons/Moisissures et Algues

Plusieurs métaux lourds dont le mercure, le cuivre, le plomb, le cobalt et le cadmium se portent à cette étude. Le choix du métal à traiter déterminera subséquemment le choix du procédé et du biosorbent.

Nous avons proposé un procédé schématique pour un laboratoire pilote afin de récupérer l'uranium par bioadsorption à l'aide d'un mycelium de Champignon/Moisissure. Le procédé candidat se définie comme suit: procédé de filtration sous-presse ou le microorganisme est attaché au filtre (en série de trois) et le débit de la solution à filtrer étant de 4 litres/minute. La solution candidate à filtrer proviendrait de mines d'uranium (Denison Mines, Elliot Lake, Ontario) suite au procédé d'extraction et de lessivage de la masse microbienne sous-terraine.

Conclusions et Recommendations

Nous croyons que sufisamment de données sont disponible pour appuyer les démarches nécessaire à l'implantation des procédés schématiques proposés. Nous proposons donc de passer à la phase II du programme en suivant certaines recommendations:

1. Planification et construction d'un laboratoire pilote. Etudes approfondies concernant la sorption de l'uranium le découplement, les vitesses à laquelle ces opérations se font ainsi que les caractéristiques de la biomasse s'appliquant au débit.

2. La biomasse candidate devrait-être soumise à des essais rigoureux, jusqu à 50 cycles utilisant de l'uranium synthétique en solution. Une analyse de la perte de la biomasse, de la dégradation lors du transfer ainsi que les propriétés du débit seraient effectuée.

3. Les essais sur les solutions synthétiques devraient être suivies par des essais sur les solutions réelles provenant de l'industrie minière.

4. Une deuxième biomasse candidate devrait aussi être analysée.

5. Une firme d'ingénieurs devrait être impliquer tout au cours des essais en laboratoire et ainsi obtenir des données préliminaires pour la construction d'un laboratoire sur place (près des mines).

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BIOADSORPTION OF HEAVY METALS FROM MINERAL PROCESSING STREAMS - PHASE I

FINAL REPORT

BY

ALLELIX INC.

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources, Canada.

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BIOADSORPTION OF HEAVY METALS FROM MINERAL PROCESSING STREAMS - PHASE I

Executive Summary

Objectives

Milestone I

To critically assess the published literature on bioadsorption processes suitable for the recovery of heavy metals from solutions produced in the mining industry and identify a candidate process for which sufficient bench-scale data has been generated to permit the design of a pilot plant.

Milestone II

To design a process schematic for a pilot plant based on the candidate process identified in Milestone I.

Strategy

We adopted the following classification for candidate processes based on the nature of the biosorbent.

1. Activated Sludge (Mixed Microbial Cultures)
2. Defined Bacterial Cultures
3. Fungi and Yeast
4. Algae
5. Microbial Derivatives (Immobilized Cells, Exopolymers)

Available information on each of these candidate processes was evaluated on both process design and economic criteria. The ultimate goal of this program is to develop a process(es) which can benefit the Canadian mining industry. Technical factors were the major consideration in this study but, the economic and practical aspects of each candidate process were not ignored.

The key criterion for a successful process will be the value of the metal recovered per unit cost of biomass. This economic calculation will depend on many factors. These factors are the availability and cost of the biosorbent, the feasibility of regenerating and reusing the biomass, the adsorption efficiency with actual mine-derived solutions and at the typical mine temperature, and the value of the metal being recovered.

Bioadsorption of heavy metals by microbial biomass is influenced by many factors. These factors include, the characteristics of the organism, the nature of the metal, culture conditions, the age of the culture, the uptake mechanism, the pH and temperature, the metal concentration in solution, and other cations and anions, and the presence of organic residues (toxic to cells) from the extraction procedures. All these factors will be considered for the process design and operation.

Discussion of Results

There are two uptake mechanisms known to occur in microorganisms. Bioadsorption, the passive physico-chemical uptake of heavy metals from solution is considered more suitable for process design. The uptake is generally rapid in bioadsorption and the metal can be recovered so that the biosorbent can be reused. In contrast, bioaccumulation, the active intracellular accumulation of metal by metabolizing organisms, is limited in economic potential because the metal cannot be recovered without destroying the biosorbent.

Our assessment of the published literature reveals that there are deficiencies in data that may have an impact on process design feasibility.

1. Biosorbents have not been evaluated adequately with test solutions that resemble actual mineral processing liquids.

2. With the exception of uranium, data on the regeneration of heavy metals from the biosorbents have not been investigated or documented.

3. The supply or generation of adequate amounts of biomass and the concomitant requirement for nutrients has not been considered.

4. There are no published process schematics or mass balance calculations.

However, we feel that the process design can be developed based on the available data with some peripheral confirmation studies.

We propose that for future work, the candidate processes be categorized according to the metal being recovered. The best target element for process design, at this time, is uranium based on its good bioadsorption behaviour and the relative ease and efficiency of its regeneration from a biosorbent.

We rank the various biosorbents for the recovery of uranium as follows.

1. Fungal Mycelium
2. Microbial Derivatives (Immobilized Cells, Exopolymers)
3. Mixed Microbial Cultures (Activated Sludge)
4. Yeasts or Defined Bacterial Cultures
5. Algae

Selected fungal species have been shown to have a high uptake capacity for uranium(VI) in aqueous solutions. The uranium can be recovered efficiently by washing the metal-laden biomass with the dilute solutions of carbonate salts (e.g. 0.1M sodium carbonate solution). Both of these attributes are desirable for a bioadsorption process.

Factors to be confirmed include the adsorption behaviour of the biomass for uranium in the presence of high concentrations of mixed cations and anions, (characteristic of mine process liquids); the physical characteristics of the biosorbent and hence its handling properties; the long-term durability of the biosorbent; and the process economics of production. These factors will depend on the fungal species selected and its availability and source (e.g. by-product of the fermentation industry).

The other candidate processes are not as far advanced, so for the recovery of heavy metals other than uranium, we rank the biosorbents as follows.

1. Defined Bacterial Cultures
2. Mixed Microbial Cultures (Activated Sludge)
3. Microbial Derivatives (Immobilized Cells, Exopolymers)
4. Fungi and Algae

Any of the heavy metals including mercury, copper, lead, cobalt and cadmium can be selected for study. The choice of metal will determine the subsequent choice of both the mineral processing liquid and the preferred biosorbent.

We have proposed a process schematic for a pilot plant for the recovery of uranium by bioadsorption with fungal mycelium. The candidate process is a filter press process with the fungal mycelium clamped in filter presses - three in series - and the feed solution flowing through the presses at a rate of 4 lit/min. The candidate feed solution will be the liquor from an underground microbial heap leach process for the extraction of uranium from Denison Mines, Elliot Lake, Ontario.

Conclusions and Recommendations

We believe that there is adequate data available to support engineering design from the proposed process schematics. Hence, we recommend proceeding to Phase II of this program with the following guidelines.

1. A pilot plant following one of the suggested flowsheets should be designed and constructed. Back-up bench scale work should be performed to confirm the respective uranium sorption and stripping isotherms and rates, as well as the flow properties of the chosen biomass.

2. The candidate biomass should be subjected to testing in the pilot plant up to 50 cycles using a synthetic uranium-containing solution. Loss of biomass, degradation of transfer and flow properties will be followed.

3. Testing on synthetic solution should be followed by trials using a typical plant isolate.

4. A second candidate biomass should be investigated and tested.

5. An engineering company should be involved throughout the pilot plant test work to observe and obtain preliminary design data for the construction of an on-site operation.

REPORT TO MILESTONE I

LITERATURE REVIEW

Allelix

BIOADSORPTION OF HEAVY METALS FROM MINERAL PROCESSING STREAMS

Phase I

Report to Milestone I

Literature Review

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BIOADSORPTION OF HEAVY METALS FROM MINERAL PROCESSING STREAMS

PHASE I

REPORT TO MILESTONE I

LITERATURE REVIEW

SUMMARY

A review has been completed of the literature pertaining to bioadsorption processes for the recovery of heavy metals from solutions produced in the mining industry. The objective is to determine if there are sufficient data published in the literature to permit the design of a pilot plant. Our evaluation has concentrated on the degree to which the data from bench-scale experiments meet the criteria for a pilot-scale process. Practical and economic factors have also influenced the selection of the most promising candidate process.

Based on available data, the recovery of uranium from dilute process liquids, using fungal mycelium as biosorbent, is recommended for pilot-scale studies. This process matches most closely our selection criteria. Several candidate processes are identified to show promise for the recovery of other heavy metals but these techniques will require more extensive laboratory investigations.

Allelix Inc.

BIOADSORPTION OF HEAVY METALS FROM MINERAL PROCESSING STREAMS

PHASE I
REPORT TO MILESTONE I
LITERATURE REVIEW

1. INTRODUCTION

This report covers the literature review in accordance with the specifications of DSS File No. 26SQ.23440-3-9139.

2. OBJECTIVE

The objective of Milestone I is to determine if there are sufficient data published in the literature to permit the design of a pilot-plant process for the bioadsorption of heavy metals from mineral processing streams.

3. LITERATURE REVIEW

A computer-assisted literature search on the bioadsorption of heavy metals from aqueous solutions was done. The keywords used and the data bases searched are shown in Appendix I. Key articles were collected and secondary references were then consulted. The bibliography (Appendix II) contains all references which we consulted.

4 STRATEGY FOR THE EVALUATION OF PROCESS DATA

In order to design a pilot-scale process the bench data must define the key operating parameters for each unit operation in the process. Moreover, to permit reasonable correlation with pilot-scale operations, laboratory experiments must have been done at sufficient scale and on a representative test solution, i.e. a mineral processing liquor containing the heavy metal or metals.

Our evaluation will concentrate on the process-design aspects. An important factor, in the design of a trial system, will be the candidate metal or metals to be removed and the source of the process stream. The chemical composition of a process stream from a different ore and a different type of extraction process will vary. In order to optimize the efficiency, a bioadsorption process should be tailored to the composition of the process liquor. Thus, we will indicate which metals appear to be the most promising candidates.

An important decision on what constitutes "sufficient" technical data had to be made. None of the literature sources identified to-date, has included a process schematic. This reflects the level of development in the technology. Our strategy, therefore, is to identify the possible unit operations (and their related technical parameters)(Table I) and select from the list the appropriate operations to assemble a hypothetical flow diagram for each candidate process (Appendix II). In some processes, several of the unit operations may be combined into a single operation. These schematics have only been used to guide our assessment of the literature data and they do not represent process prototypes.

The ultimate goal of this biotechnology program is to develop a process or processes which can benefit the Canadian mining industry. We believe that bioadsorption for mining applications is technically feasible. However, the economic and practical aspects of a candidate process relative to the Canadian mining environment must be considered. The process should use a "biosorbent" which is readily available and whose "delivered" price at the mining site is economical. The operating characteristics of a process should be realistic from both the technical and economic standpoint e.g. high adsorptive capacity for metals and/or efficient recovery of metal(s) per unit cost of biosorbent; operation at temperatures compatible with mining situations; and the ability to accomodate large volumes of feed solution per day. Processes considered by us to be questionable for one or more of these reasons have been ranked below those processes or concepts which we consider to be more compatible with mining operations.

The assessment of bioadsorption processes requires some understanding of the mechanisms by which microorganisms accumulate and concentrate heavy metals from their immediate environment. A brief overview of the mechanisms of uptake of heavy metals by microbes is warranted.

5. THE CONCENTRATION OF METALS FROM SOLUTION BY MICROORGANISMS

The ability of certain bacteria, fungi and algae to accumulate and concentrate metals has long been recognized. Much of the research has focused on the potential use of these organisms as indicators of heavy metal pollution in the environment. Some organisms have been shown to accumulate metal contents as high as 36-40% by dry cell weight. However, the mechanisms that enable these organisms to survive and grow in the presence of metal concentrations, which are toxic to other organims, have also been studied. Significant variations are noted between the metal-uptake ability of different genera, different species, and also different strains within a species. Metal tolerance may reflect the ability of an organism to accumulate high concentrations of metal without dying. Alternatively, metal tolerance may be due to an organism's ability to prevent the intracellular build-up of metal concentrations toxic to its metabolic processes.

The uptake of metals by microorganisms is a two-stage process. The first phase occurs very rapidly in most organisms i.e. within 5-30 min. of cell contact with the metal-containing solution, and involves the "passive" physicochemical adsorption/retention of metal cations and anions by the constituents of the cell wall. This "passive" process we define as bioadsorption. A second phase involves the "active" physiological absorption of metals via energy dependent metabolic processes. This latter phase, which we identify as bioaccumulation, is dependent on the tolerance of the specific organism to relatively high concentrations of "toxic" elements in the intracellular cytoplasm and other subcellular components. Any compound of natural origin, which can be used to remove heavy metals from a solution, will be called a biosorbent or adsorbent.

The efficiency of metal concentration from an aqueous solution, depends on the physiology of the microorganism. It is also influenced by the chemistry of the metal; the concentrations of other metals and anions in the solution; the element concentration in solution; the age of the cells; the pH and the temperature. These aspects will be discussed later.

6. EVALUATION OF BIOADSORPTION PROCESSES

We have classified the potential processes according to the nature of the biosorbent. The following headings have been selected:

1. Activated Sludge
2. Defined Bacterial Cultures
3. Fungi and Yeasts
4. Algae
5. Microbial Derivatives.

There is some overlap of the information for these processes but specific attributes of each type of adsorbent warrants a separate assessment.

Our assessment of the bioadsorption technologies for mining processes indicates that there are still many questions to be answered. They include:

a) How available is the biosorbent?
b) How reproducible is the biosorbent especially it if is not produced from a defined microbial culture?
c) Can the biosorbent be produced on-site?
d) Does production require expensive nutrients, high energy input (heat, light), etc.?
e) Can the biosorbent be readily recovered from the system i.e. flocculation, sedimentation, etc.?
f) Can the biosorbent be regenerated and reused?
g) If it cannot be regenerated, how is/are the metal(s) recovered?
h) What waste treatment facilities will be required?

i) How well defined are the operating parameters for the bioadsorption stage (pH, temperature, biomass/liquid ratio)?

j) How well defined are the methods to produce derivatives or extracts from the microorganisms?

k) What is the economic feasibility of a more sophisticated type of biosorbent e.g. immobilized cells?

l) What are the effects of organic residues from ore-processing methods upon the efficiency of the bioadsorption process?

m) How significant is competition from other cations and anions in the mineral processing liquor upon the efficiency of the bioadsorption process?

The distinction between bioadsorption and bioaccumulation is important in process design and has been poorly described by many researchers. Bioadsorption and bioaccumulation have often been combined into the single heading of uptake because the predominant mechanism in effect is not known. Bioaccumulation, which is the predominant uptake mechanism in many organisms, is less desirable in process design because it requires that the cells be actively metabolizing and the poor release of heavy metal from the intracellular matrix makes it difficult to reuse the biosorbent. Bioadsorption, on the other hand, involves the chelation/deposition of metals on the cell surface. The uptake is generally rapid and it is easier to recover the metal(s) and reuse the biosorbent. Although we shall not ignore bioaccumulation we shall, however, concentrate on the latter mechanism which is better suited to process development.

Two basic alternatives are available for bioadsorption processes. One approach involves a single-stage procedure with actively growing, metal-tolerant organisms in the ore processing stream, fortified with appropriate nutrients. The second approach involves producing the biomass in a separate reactor, and then bringing the isolated microbial biomass into contact with the process liquor in a controlled environment i.e. a two-stage concept. The biomass may be used as produced, deactivated before use, treated to improve physical characteristics (e.g. immobilization), or extracted to yield purified components with high complexing ability.

The use of actively growing cultures (i.e. combined bioadsorption/ bioaccumulation) is more compatible with processes based on large storage systems or lagoons which are exposed to the natural elements. This approach has many limitations. Low temperatures cause low growth rates during winter, and evaporation during summer affects metal-concentrating efficiency. Expensive storage facilities and lack of space at mine sites make this approach uneconomical. More compact systems that can be operated in controlled environments, with high adsorption of metals by biosorbents at short residence times, would be preferable. Where nutrient supplements are required, it is imperative that the amount is minimal. Otherwise, the cost of nutrients will render a process totally uneconomical. This limitation may also apply to the microbial biosorbent produced in a separate reactor, although the volume of liquid will be much less. If a biosorbent is a by-product of another process e.g. municipal activated sludge or spent fermentation mycelia, the biosorbent may be relatively "inexpensive". However, other factors such as its availability, its reproducibility from batch to batch and the cost of collecting and shipping adequate amounts of it to the mine sites will affect its value.

The attractive feature of bioadsorption is a certain specificity of the biosorbent for the divalent and multivalent heavy metal cations. As noted earlier, the metal uptake may vary widely for different mutant strains within a species and between different genera. The nutrient status of the organism, the age of the cells, the temperature, pH, etc. are all important parameters affecting the performance of a biosorbent. Another factor is whether enough biomass can be generated at an economical cost to meet the needs of a process. This introduces the question of what might the daily requirement be for a biosorbent. We will consider a hypothetical case.

A mineral processing plant might generate 15×10^6 L/day of process liquid. If we assume that copper is the only element present in this liquor at a concentration of 10 mg/L, this would be equivalent to a daily copper

loading of 15×10^4 g/day. A realistic uptake efficiency of copper by microbial cells is 10% (dry weight basis). To treat the above volume of liquid (ignoring at this stage the adsorption characteristics) would require 1500 Kg of dried cell mass per day. As an approximate biomass value this would require the nutrients (BOD) or daily sewage volume from a community of approximately 40000 (an inexpensive source of nutrients). It should be noted that this calculation does not take into account any reduction of adsorption efficiency due to other cations and anions and/or other interfering compounds present in the liquor.

Bearing these observations in mind, we shall review the status of the candidate adsorption processes and their applicability to the mining industry.

6.1. Activated Sludge Systems

a) The State-of-the-Art

For the purpose of this study, we define activated sludge (AS) to be a biosorbent consisting of a naturally selected, undefined, mixed culture of microorganisms. In addition to bacteria, the biological constituents will include algae, fungi, ciliated protozoa, rotifers and nematodes.

At first glance, AS systems, which are applied normally to the reduction of the organic content of wastes, do not seem suited to the mining industry. However, their ability to remove heavy metals from municipal sewage has long been recognized and AS systems are probably the best characterized of any of the bioadsorption processes. Most of the developments using pure cultures of microorganisms and isolated microbial polymers are, as will be discussed later, based on the behaviour of microorganisms in AS processes.

Data generated in municipal waste treatment plants have sparked much of the interest in the mechanisms of metal removal by AS systems. Caution is advised, however, in assessing the removal efficiencies for different metals. At the typical operating conditions (pH, temperature, etc) in a sewage treatment facility, elements such as cadmium, copper, chromium,

manganese and lead may be present predominantly as particulates e.g. as high as 90% (Nielsen and Hrudey, 1983) and the high removal efficiencies of 92-93% may be due solely to a filtration effect rather than to bioadsorption. Nelson et al. (1981) stated that only 5-20% of the heavy metal removal in a waste treatment system was by filtration of metal particulates in the primary sedimentation stage of the process and that depending on the individual characteristics of a metal, 10-80% of the metal removal occurred in the AS stage. They showed in laboratory experiments, that when cadmium, copper and zinc were spiked as soluble salts into aerated synthetic sewage liquor + AS (metal concentrations, 0.5-1.5 mg/L), the uptake of metal was rapid and essentially complete within 1 hour. The efficiencies of adsorption were 80 - 93% and the speed of the reaction indicated that the principal mechanism was the "passive" bioadsorption. It was noted that the pH influenced significantly the adsorption process and the age of the cells was also an important parameter. At pH 7.0, the relative affinity of metals for five day old AS (i.e. the mean residence time of cells in the digester) was Zn>Cu>Cd. In the case of one day old AS, the relative affinity for metals was Cu>Cd>Zn.

Neufield and Hermann (1975) shock dosed batch samples from an AS culture in synthetic sewage medium. Mercury, cadmium and zinc were each added at concentrations ranging from 30-1000 mg/L. The uptake of the metals was very rapid at all concentrations and essentially complete after 1-3 hours. The adsorption efficiencies at lower concentrations (<300 mg/L) were 90-95% (Hg), 70-80%(Cd) and 43-60% (Zn). At high concentrations (1000 mg/L) the mercury uptake was of the same order as above, but the adsorption efficiencies for cadmium and zinc dropped significantly (e.g. approx. 40%) indicating a saturation of adsorption sites. The rate of reaction again suggested a surface bioadsorption process. Other authors (Ghosh and Zugger, 1972), at mercury concentrations of 5 and 10 mg/L added to AS cultures, noted uptakes of only 51 and 58% respectively.

Cheng et al. (1975) also confirmed that cadmium added to AS cultures in synthetic medium was rapidly adsorbed (within 10-30 min.). Element concentrations of 2.07, 10.3, and 25.5 mg/L were adsorbed at pH 6.7 with

efficiencies of 85%, 92% and 75% respectively. Other metals showed similar patterns of uptake e.g. copper (81-84% within 10 min.), lead (95-97% - 10 min) and nickel (47-59% - 10 min). Deactivating the sludge by heat sterilization did not significantly alter the adsorption characteristics except that a secondary slower accumulative stage in the case of nickel was not present in the deactivated cultures. These authors noted that complexing agents such as nitrilotriacetate (NTA) and ethylenediamine tetraacetic acid (EDTA) interfered significantly with the adsorption of copper.

Stoveland and Lester (1980) reviewed many of the factors affecting the removal of heavy metals by AS. Brown and Lester (1979) had earlier concluded that the production of extracellular polymers by the AS organisms contributes significantly to the metal uptake. Sites for the interaction of metals in the AS include both the polymers released into the supernatant as well as the cell capsules. Casey and Wu (1977) observed that the formation of cell capsules in an AS system was increased under conditions of phosphate limitation. In laboratory studies with AS, cells grown in a synthetic medium having a COD/P ratio of 2000:1 gave the most rapid and efficient uptake of cadmium and copper (acclimated cells were shock dosed with concentrations as high as 280 mg/L). Adsorption was complete for both elements within 10 min. of the addition of the metal. The removal efficiencies were approximately 50%. It was also noted that the adsorption of copper and cadmium was proportional to the metal concentration in solution i.e. the data conformed to Freundlich and Langmuir adsorption isotherms. This will be important in the design of adsorption processes.

The role of extracellular polymers was reviewed by Brown and Lester (1979). In studies with AS in synthetic medium (pH 7.4-7.7), Sterritt et al. (1981) found that the bioadsorption of lead, chromium $^{(3+)}$ and copper was not affected by the age of the cells. The removal of metals appeared to be due primarily to low solubility. If polymers were largely responsible for the metal adsorption, it was expected that older cultures with proportionally higher concentrations of polymers (Brown and Lester, 1982b) would be more effective adsorbents. They found that the older the sludge (up to nine days)

the higher the concentration of exopolymers in the AS mixed liquors. These authors noted, however, that the most efficient uptake of metals occurred with the three day old sludge. Tests to compare the ability of whole cell flocs, polymers extracted from flocs and extracted cells (polymer depleted) to complex cadmium and nickel indicated that the extracellular polymers were efficient complexing agents for cadmium and, therefore, played a significant role in the complexation of that metal by whole cells. The polymers were less important to the uptake of nickel. (Brown and Lester, 1982a).

Dunn and Bull (1983) noted that with an AS mixed culture (or community) in a laboratory reactor, the major portion of the copper adsorbed was on to those cells adhering to the glass surfaces (30 $\pm$ 6% of dry weight for the adhering bacteria as compared with 0.92 $\pm$ 0.2% for free cells). A similar effect was also observed by Remacle (1981) with a mixed AS culture in a continuous flow reactor. When the medium was spiked with cadmium, the adsorption of cadmium was higher (0.61% per cell dry weight) for bacteria adsorbed on to the wall of the reactor compared to 0.13% Cd for free cells. In this case, the younger cultures were again more active adsorbents and they observed that the film of bacteria was more stable in a carbon-limited culture medium.

AS biomass (preconditioned and dried) was shown by Tzesos and Keller (1983) to adsorb Radium-226 with an impressive concentration factor (11000 to 40000). The efficiency of uptake was apparently dependent on the source of the AS. The recovery of the element was not discussed. Volesky and Tzesos (1982) identified that AS from different sources could take up uranium and thorium. AS was not, however, as effective an adsorbent for these elements as Rhizopus arrhizus biomass. Uptake capacity for AS varied with the source of the AS, the element, and the concentration of the element in solution.

Shumate et al. (1980) operated a fluidized-bed reactor system utilizing a mixed culture of actively growing, denitrifying bacteria adsorbed on to 30-60 mesh anthracite coal. At an operating temperature of 25^{0}C, the

uptake of uranium by this culture was rapid with the saturation level for the biosorbent being approximately 14% of dry cell weight. The uptake was independent of temperature in the range 25-50°C. These authors noted that this reactor operated in the countercurrent mode could reduce the uranium concentration in a liquid stream from 25 g/L to 0.5 g/L in a mean residence time of 8 min. No data were presented for the recovery of the uranium from the biomass.

The data, as a whole, indicate that bioadsorption is an important process for the uptake of metals such as mercury, cadmium, lead, copper, cobalt, radium and to a lesser extent zinc, nickel, uranium and thorium by activated sludge(AS). Very efficient adsorption levels have been noted.

b) Process Evaluation

A bioadsorption process based on activated sludge would follow the Model 1 Schematic (Appendix II) with the probable modification that the biomass be produced in a separate reactor prior to treatment of the ore-processing liquor.

We have not identified any bioadsorption process utilizing activated sludge to adsorb metals from ore-processing streams. We believe, however, that this approach or its refinement using defined microbial species (see 6.2) should be investigated.

Attractive features of this biosorbent include:

i) Bioadsorption is the predominant mechanism for the uptake of heavy metals such as mercury, lead, cadmium, copper and cobalt by activated sludge.
ii) The bioadsorption is a rapid process.
iii) Deactivation of the sludge is not necessary.
iv) The natural selection process of activated sludge systems leads to a predominance of "hardy" strains of organisms.
v) The organisms do not require a highly defined culture medium e.g. sewage from the mining community would serve as one nutrient source.

Before a pilot-scale operation could be designed, it would be essential to undertake laboratory studies to define more precisely the operating parameters for unit operations. Decisions to be made and information needed include:

i) Selection of target metal or metals.
ii) Selection of ore-processing method and the appropriate process stream which will serve as the test solution.
iii) Adaptation/acclimation of activated sludge culture.
iv) Evaluation and optimization of the bioadsorption efficiency/kinetics with process liquor. e.g. effect of pH, temperature, contact time, age of biomass, nutrient requirements, effect of competing cations/anions, effect of chelating agents in the process liquor.
v) Evaluation of the efficiency of biomass recovery (filtration, sedimentation, particle size, etc.).
vi) Tests to evaluate procedures to recover the metals from biomass.
vii) Adsorption capacity of regenerated biomass as well as physical characteristics.

The information in the literature indicates that bacteria, which have capsules or slime layers or which liberate polymers into the surrounding solution, are the more effective biosorbents. They tend to grow attached to the surfaces of reactors. If metal-laden sludge can be regenerated, the preferred process would be the two-stage one, incorporating a separate reactor to produce the biosorbent.

We advocate that serious consideration be given to the incorporation of a rotating biological contactor (RBC) in a process design. The RBC is a modified activated sludge process in which the liquid being treated flows at a controlled rate through the lower section of a horizontal reactor. The lower section is divided by transverse partitions into several compartments and liquid flows between the compartments through small holes in the dividers.

The design of the reactor is such that the flow of liquid through the reactor is similar to that in a plugged-flow system. Compartments farthest from the inlet receive feed solution which has already been depleted of nutrients (or of metals in a bioadsorption process). The adsorption equilibria and kinetics characteristic of the activated sludge/metal interaction would favour the use of a plugged flow reactor to achieve a high efficiency of metal removal. The biological floc or adsorbent in an RBC grows attached to screens which are rotated in a transverse direction to the flow of liquid. The rate of rotation determines the relative time that the floc is in contact with the process liquid. During the remainder of a rotation cycle the floc is exposed to air above the surface of the liquid. RBC units are enclosed which will facilitate more accurate temperature control in the field. The RBC reactor design gives high biomass yields, promotes the growth of surface adhering bacteria, affords a high ratio of cell surface to volume of process liquid, and generally achieves a very high efficiency for removal of suspended solids. We believe that the same levels of efficiency can be attained for the removal of metals.

6.2. Defined Bacterial Cultures

a) The State-of-the-Art

This concept is a refinement of the activated sludge process. The major goal is to isolate bacterial species with enhanced capacities to adsorb heavy metals. The most successful sources for such organisms have been either activated sludge or metal-polluted soils in which exposure to toxic metals has already induced a natural selection process favouring metal-tolerant strains. It is assumed that metal-tolerant organisms will accumulate the metal to a high degree. This is not necessarily correct. The inability to take up a toxic metal from the surrounding medium may be an organism's defence mechanism. Metal tolerance in a bacterium may be due to either its ability to withstand the presence of high concentrations of a metal in the intracellular cytoplasm i.e. bioaccumulation. On the other hand, the precipitation/chelation of the metal at the cell wall i.e. bioadsorption, prevents the metal reaching sensitive intracellular components (Wood and Wang, 1983).

Caution is also required in assessing the usefulness of an organism as a biosorbent based on its high uptake of a metal per unit weight of cell mass. From the standpoint of process design, the most important criterion is not the absolute metal uptake by the cell but rather the overall metal-adsorption capacity of the biosorbent i.e. weight of biomass x concentration of metal adsorbed on biomass. This value is a more accurate indicator because metal-tolerant organisms may have much reduced growth rates in the presence of the toxic metal.

With the exception of one organism, a strain of Zooglea ramigera (isolate 115), (Dugan and Pickrum, 1972), test data have not been published on the behaviour of metal-accumulating organisms in liquors of similar composition to that of mine process streams. Most of the studies to-date have used highly defined culture media which are not relevant to the mining situation. Many bacteria and fungi have been screened for their uptake of specific metals such as copper, lead and cadmium. (Horitsu et al, 1979; Macaskie and Dean, 1982; Horitsu et al., 1978; Aickin and Dean, 1979). Bioaccumulation, however, appears to be the predominant mechanism of uptake.

Passive uptake by "resting" cells of some organisms may indicate promising adsorbents for certain metals. Certain strains of Citrobacter sp. and Pseudomonas fluorescens (as resting cells) could adsorb lead from buffered solutions (300 mg Pb/L) to 10-11% of cell dry weight (Aickin and Dean, 1979). It was noted that the addition of glycerol-2-phosphate to the lead/buffer solution stimulated the bioaccumulation mechanism and these "resting" cells could then adsorb lead as efficiently as growing cultures. Older cells (late logarithmic phase or stationary phase of growth cycle) gave the better uptake when tested in that resting state.

Until more complete data are available on the rate of uptake of the respective elements, the adsorption isotherms, the rate of production of biomass relative to the total metal adsorption capacity, and the performance of these organisms in more realistic test conditions, it would not be

justified to use such organisms in a pilot-scale process. The approach of most research groups has been to identify candidate organisms for subsequent laboratory investigations into their usefulness in future bioadsorption processes.

Several organisms isolated from activated sludge systems have provided promising data. Z. ramigera 115 biomass has been shown to adsorb copper, cobalt, iron and nickel from distilled water within 18 hours (Friedman and Dugan, 1968). Cell mass (0.1 g dry weight) could adsorb 99.3% of the cobalt present initially at 500 mg/L in 50 mL of solution and 84.9% of copper (initial concentration in 50 mL - 800 mg/L). The bioadsorption of nickel was less efficient. The authors also noted that the age of the cells influenced significantly the adsorptive capacity. This appeared to be related to the extent of development of the gelatinous zoogleal matrix surrounding the cells. Temperature influences the synthesis of this gelatinous matrix. Dugan and Pickrum (1972) noted that when cultures of Z. ramigera 115 were at the stationary phase of the growth cycle, polysacchrarides constituted 90-98% by weight of the cell floc. These authors tested the ability of the cell floc to remove cations and anions from several mine waters (pH 3.0). They estimated that 25-33% of all cations analyzed and 25% of the sulphate were adsorbed by the cell floc. Data were not presented for the heavy metal cations. Dugan and Pickrum also tested the cell floc for its adsorption capacity on synthetic mixtures of copper, cobalt, ferric iron and nickel in aqueous solution (as their chlorides). Iron was always strongly adsorbed but the efficiency of adsorption of the other cations was dependent on the respective concentration in solution and the nature of the competing metal ions. Mercury and cadmium were also adsorbed well by zoogleal cell floc but the medium used to grow the cultures influenced significantly the adsorptive capacity.

The use of cell floc to remove metal cations has been proposed again recently (Norberg, 1981) and although further experimentation is required to define more accurately the process characteristics, it is one of the more

promising techniques. Dugan and Pickrum (1972) envisaged a two-stage approach where the cell floc would be produced in a separate reactor. Although the metal uptake appears to be a mass transfer limited process (complete after generally 18 hours), the use of this organism in a biological contactor may prove feasible. However, impurities in the ore-processing stream may inhibit the production of polysaccharide.

Hatch and Menawat (1979) found that Sphaerotilus natans, another slime-producing organism common to polluted waters, adsorbed iron, cadmium, copper and cobalt in the mucilaginous layer on the cell wall by a process which was mass transfer limited. Patrick and Loutit (1972) also reported this capability for S. natans.

Both of these organisms grow well attached to surfaces. In this sense, they have the characteristics deemed desirable for organisms to be effective metal adsorbing species in a mixed activated sludge system. Studies however, would be required to evaluate the effect of nutrient sources e.g. sewage on the metal-complexing ability of the cells/cell flocs. It is important to note that cell capsules and extracellular polymers or slimes appear to play a prominent role in the bioadsorption of metals by other bacteria. Citrobacter sp., a cadmium accumulating organism, produced slimes (Macaskie and Dean, 1982). An Azotobacter sp. able to concentrate lead to 31% of its dry weight had a prominent cell capsule (Tornabene and Edwards, 1972) and more recent studies with Klebsiella aerogenes (Brown and Lester, 1982a, 1982b) have demonstrated the importance of the cell capsule/exopolymers for metal uptake by that bacterium.

Pseudomonas aeruginosa was shown to take uranium very rapidly from solution with the reaction complete in essentially one minute from the time of the initial contact of cells with solution (Strandberg et al., 1980, 1981). A total capacity of 10-15% of dry cell weight was noted for this organism and it involved an intracellular uptake. Treatment with metabolic inhibitors such as 2,4-dinitrophenol, sodium azide, mercuric chloride or formaldehyde did not affect the uptake of uranium by P. aeruginosa cells. The uptake of

uranium was relatively insensitive to factors such as pH, temperature, other cations, etc. These authors also noted that not all of the P. aeruginosa cells in the preparation adsorbed uranium. The recovery of metal from biomass was not efficient.

b) Process Design

The same limitations which apply to activated sludge based processes are relevant to this type of biosorbent.

6.3. Fungi and Yeasts

a) The State-of-the-Art

Yeasts have been investigated for their ability to adsorb metals (Norris and Kelly, 1977a, 1977b). The uptake of cadmium and cobalt by active cells of Saccharomyces cerevisiae was found to involve both bioadsorption and bioaccumulation (Norris and Kelly, 1977b). The surface binding was very rapid and independent of pH but the metal-uptake capacity was stated to be significantly less than with other microorganisms. Bioaccumulation was metabolically controlled and influenced significantly by the presence in solution of other cations. Accumulated elements could not be readily recovered by mild leaching agents such as in 1mM EDTA or dilute sulphuric acid solution at pH 2.

Shumate et al. (1978) and Strandberg et al., (1980) also investigated the metal-uptake capacity of S. cerevisiae. They found that the uptake of uranium by viable cells of this organism was by bioadsorption with little uranium being found in the cells (Strandberg et al. 1980). The overall uptake capacity was 10-15% of dry cell weight but not all of the cells appeared to adsorb the uranium. The nutrient level in the medium used to culture the cells influenced their subsequent capacity to take up uranium. Temperature and pH of solutions also influenced significantly the adsorption of uranium by S. cerevisiae. A relatively high percentage (approx. 84%) of the bound uranium could be desorbed by washing with 0.1 M ammonium carbonate solution. The regenerated cell exhibited an enhanced rate of uptake of uranium. The uptake was, however, reduced by the presence of calcium or amino acids such as glutamic acid and aspartic acid.

Fungi have shown some interesting properties. Spent mycelia from fermentation industries has been used by two research groups for the bioadsorption of uranium and thorium (Volesky and Tzesos, 1982, Nemec et al., 1977). Tzesos and Volesky (1981) found that deactivated Rhizopus arrhizus mycelium could take up uranium buffered at pH 4. The uptake of metal was concentration dependent and conformed to Freundlich adsorption isotherms.

Nemec et al. (1977), used the mycelium of Penicillium chrysogenum. They treated the mycelium to render it in a more rigid, particulate form for use in commercial processes. The observed uptake capacities for uranium were significantly lower e.g. 4-10% of dry weight depending on the stiffening agent used.

Chiu and Zajic (1976) also showed that an unidentified Penicillium sp. could adsorb uranium to a level as high as 17% of dry cell weight. They demonstrated that the uptake of metal conformed closely to a Freundlich isotherm. They obtained a correlation coefficient of 0.998.

Galun et al. (1983a) investigated the adsorption of uranium (VI) by Penicillium digitatum biomass. They used various pretreatments but the uptake of U (VI) from UO_2Cl_2 solution improved only marginally. Thus, concentrations of 1-10 mg/L as uranium could be removed with an efficiency of 75-90% within 1-4 h by 4 g (net weight) of fungal biomass. The uptake of uranium was temperature dependent. They also noted that the presence of the detergent TWEEN-80 during the cultivation of the cells improved the efficiency of uptake of metal. Galun et al. (1983b) found that the uranium (VI) adsorbed on Penicillium digitatum biomass could be desorbed efficiently (94-99%) by solutions of alkali carbonates (0.1-0.2M). The capacity for uranium uptake was increased by the desorption process. Treatment with alcohol or by boiling also improved the adsorption characteristics.

Special studies on the ability of fungi to concentrate heavy metals from their environment have also identified some interesting strains. Aickin and Dean (1977) noted, however, that the capacity of strains of fungi isolated from lead-polluted areas to accumulate lead (weight %) did not match the better bacterial cultures. An unidentified fungus did accumulate 19% lead while an Aspergillus niger strain took up 13% by weight of lead. Another A. niger strain was found to take up 15% by weight of cadmium (Doyle et al., 1971). An interesting observation was made with metal-tolerant fungi in that the uptake of copper reached a constant level above which it was independent of extracellular metal concentration, i.e. a cellular defense mechanism is involved (Baldry and Dean, 1980).

b) Process Design

From the standpoint of process design only the fungi warrant serious attention. One of the most promising technologies for the bioadsorption of uranium and other radionuclides is the use of spent fungal mycelium from the fermentation industry (Volesky and Tsezos, 1982). The adsorption of metals by fungi appears to be related to the chitin content of the cell walls (Tsezos, 1983) and the potential exists for the use of deactivated fungal mycelium as an ion-exchange material able to be reused many times over. At this stage, the data on the interaction of other heavy metals with mycelia of different fungal species have not been well enough documented to permit pilot-scale studies.

The growth rate for fungi are generally lower than bacteria. Culture requirements and nutrients are also more fastidious. This poses the question of whether or not adequate amounts of biomass would be available. The physical handling characteristics will also be important but, if the biosorbent is able to be reused, the supply of biomass becomes of lesser significance. At present, reuse would be limited to elements such as uranium and possibly radium.

6.4. Algae

a) The State-of-the-Art

Algae concentrate metals from the natural environment and show impressive accumulation or concentration factors. This factor is the ratio of the metal concentration in the biomass (mg/g cell dry matter) to the metal concentration in solution (mg/L) (Becker, 1983). Khummongkol et al. (1982) found that cadmium uptake by live Chlorella vulgaris cells conformed to the typical two stage process involving a rapid uptake (adsorption) followed by the much slower accumulation mechanism. Horikoshi et al. (1979) noted that uranium uptake by Chlorella regularis was enhanced significantly if the cells were killed by scalding. Similar differences were observed in copper uptake by live and heat-inactivated cells of Chlorella regularis (Horikoshi et al., 1977). Scalding the cells increased the rate of uptake of copper as well as the total amount of element accumulated. Also, whereas living cells only released 18% of the adsorbed copper upon elution with EDTA, 70% of the copper could be desorbed from scalded cells. Hassall (1962) noted similar differences in metal uptake by live and dead algae. Horikoshi et al. (1977) hypothesized that the heat treatment had changed the metal binding sites. It appeared that the distribution of copper favoured the insoluble cell fraction in scalded cells.

At lower concentrations, the initial uptake of cadmium by Chlorella vulgaris (i.e. bioadsorption) is proportional to the metal concentration and conforms to Freundlich or Langmuir isotherms (Khummongkol et al., 1982). The uptake of metals by algae is also influenced significantly by the presence of other cations (Sakaguchi et al., 1980) and anions such as phosphate (Khummongkol et al., 1982). Metal uptake is often combined with an equivalent release of potassium (Gale and Wixson, 1979).

The green alga, Cyanidium caldarium is considered a promising biosorbent. It is both thermophilic and acid-tolerant (Wood and Wang, 1983).

b) Process Design

Algae have been proposed as biosorbents to remove heavy metals from wastewater (Filip et al., 1979). The most successful applications have involved tailings ponds and meander systems (Gale and Wixson, 1979) and this combination serves to overcome the major limitation of inadequate light intensity. Shallow water systems, large surface areas, adequate light intensity and a suitable nutrient source will foster the growth of algae blooms (Gale and Wixson, 1979). Brierley and Brierley (1983) examined the feasibility of using algal growth in a tailings pond to remove 0.8 mg/L each of uranium and molybdenum from a mine effluent. Based on a daily volume of 15×10^6 L, they calculated that the area of the pond (or equivalent illumination flux) would have to be increased from 0.15 hectares to 17.5 hectares. Becker (1982) reviewed the limitations of using algae to remove heavy metals. He estimated the maximum possible yield of an algal culture to be 20-40 g dry weight of cells/m^2/day or 200-400 Kg/hectare/day. Assuming a metal uptake capacity of 10% of dry weight, 20-40 g of dry weight biomass would only remove 20-40 g of metal (i.e. treat 4000L of solution containing 10 mg metal/L), so the feasibility of using growing algae for direct treatment of streams is very poor.

The ability to reuse algal biomass is the key to the practical use of algae to remove heavy metals from the large daily volumes of mineral processing liquids. The use of algal derivatives as biosorbents (next section) may improve its value but, we do not consider that an economical and practical process can be designed at this time using such a biosorbent.

6.5. Microbial Derivatives

This section will cover essentially two types of product. They are immobilized cells and metal-chelating compounds (e.g. gelatinous polymers, polysaccharides) extracted from microbial cultures. The common goal of these separate approaches is to prepare a chemical product, of natural origin, with a higher metal-complexing ability than crude biomass preparations. It should be in a form that is reusable so that its cost per unit of metal recovered is significantly reduced.

6.5.1. Immobilized Cells

a) The State-of-the-Art

Bacterial and algal cells have both been immobilized in gel supports. Nakajima et al. (1982) found that when Chlorella regularis and Streptomyces viridochromogenes cells were embedded in different gel supports, the adsorption of uranium by the immobilized cells relative to the support composition decreased in the order toluene diisocyanate method or glutaraldehyde method >polyacrylamide method > agar method >cellulose acetate method > alginate method. Polyacrylamide was selected because of its prior commercial use in other immobilized systems.

The authors demonstrated that a column of Streptomyces cells, immobilized in polyacrylamide, adsorbed uranium quantitatively (20 mg/L) from aqueous solution. The uranium was desorbed readily by 0.1M sodium carbonate solution. Over the course of five adsorption/desorption cycles the dry weight of the immobilized cells decreased by 2%. This was significantly better than the 50% loss in dry weight observed with free Streptomyces cells subjected to five adsorption/desorption cycles. Chlorella cells appeared to behave in a similar fashion. No data were presented for the ability of the immobilized cells to adsorb/desorb other heavy metals.

Aickin and Dean (1979) immobilized active bacterial cells (Citrobacter sp.) in polyacrylamide gel. A column containing 0.5 g (dry weight) of cells could accumulate 715 mg of lead from 2.75 L of solution percolated through the column. The lead concentration was 500 mg/L and glycerol-2-phosphate was required for efficient uptake of lead i.e. a bioaccumulation reaction. Lead was taken up only to a small extent in the absence of phosphate. No desorption methods were reported but it was noted that on storage,the cells'ability to remove lead decreased significantly i.e. loss of viability of the cells?

A variant of the immobilization approach is the use of chemically stiffened fungal mycelium. This type of biosorbent has been patented for application to the recovery of uranium and radionuclides (Nemec et al., 1977). These authors caused various polymeric compounds to condense/polymerize on the surface of either wet or dried fungal mycelium (Penicillium or Aspergillus spp.). The stiffened product was granulated for use and was claimed to be "essentially water-insoluble". The data in the patent refer only to the adsorption of uranium. It is stated that the adsorbent will remove lead. There is however, no indication of whether or not the lead can be desorbed for regeneration of the adsorbent.

b) Process Design

At present the available data are inadequate to design a pilot system which uses these advanced biosorbents. With free cells or mycelia, major difficulties with a pilot system may be encountered in the production and physical recovery of biomass or metal-laden biomass. Costs of producing biosorbent may be significant. However, immobilization of cells by entrapment or stiffening is a realistic approach to improving the physical characteristics of the biomass. This will assist its use in column reactors and the reusability should improve the economics.

We believe that this concept should be investigated further. However, present data do not define many important process related factors including:

a) the conditions/reagents needed to desorb heavy metals (other than uranium);

b) the effect of desorbing agents on the physical characteristics of the adsorbent;

c) the stability of the immobilized biosorbents in the presence of high ionic strength solutions and organic compounds/solvents liable to be encountered in mineral processing streams;

d) the effects of temperature, pH variations on the biosorbent;

e) the effect of immobilization on the metal-adsorption capacity and the kinetics of adsorption;

f) the economics of the immobilization procedures, i.e. how much metal/solution can be recovered/treated per unit cost of immobilized biomass?

An additional factor of concern is to design the process system to accept the presence of fine particulate slimes in the feed solutions.

6.5.2. Microbial Polymers

a) The State-of-the-Art

The ability of many organisms to adsorb heavy metals has been closely linked with extracellular polymers released into the supernatant solutions or polymers present in the capsules surrounding the cells (Sterritt and Lester, 1979; Friedman and Dugan, 1968; Corpe, 1975). Sterritt and Lester (1979) considered these polymers to be particularly important in the removal of heavy-metals by activated sludge systems.

It has been demonstrated that microbial polymers (usually anionic or cellulosic-type polysaccharides) can efficiently bind heavy metals (Corpe, 1975; Brown and Lester, 1982; Dugan and Pickrum, 1972; Strong et al., 1982). Significant proportions of these complexes will remain water soluble.

It has been proposed that microbial polymers can be used to recover metals from mine drainage (Dugan, 1970; Dugan and Pickrum, 1972). However, in their studies they used the cell flocs of Zooglea ramigera 115 rather than the extracted polymers. Norberg (1981) recommended the use of this floc to treat acid mine water and it is reported (Brierley and Brierley, 1983) that the metals could be recovered from the gel by acid extraction. It is not indicated whether the cell floc was reusable.

Other natural polyelectrolytes have also been proposed for heavy metal removal. These include polygalacturonic acid (Jellinek and Sangal, 1972), chitin and chitosan (Elson et al., 1980), chitin phosphate and chitosan phosphate (Sakaguchi et al., 1981), and emulsan and emulsansols from Acinetobacter.RAG-1 (Zosim et al., 1983). All of these compounds are very specialized and are currently very limited in supply or expensive to produce.

b) Process Design

The use of natural polyelectrolytes from organisms is an advanced concept. As with immobilized derivatives, considerable information still has to be obtained before these compounds can be used in a process. To be practical, the isolated polyelectrolytes must recover economical amounts of metal per unit cost of adsorbent and be competitive with synthetic ion-exchange resins. To achieve this goal, the compound must be reusable many times over, the losses during use must be low, and the physical characteristics of the polymer must make it easy to manipulate and recover from a process. There are no data in the literature to demonstrate the adsorption characteristics of these polymers in complex mine processing liquors, and competition from other cations may be severe e.g. Ca, Mg, Fe.

At present, the most practical way to use these polyelectrolytes is in natural association with the cells. However, there is considerable scope for future development. The isolation and culture of microbial strains that produce higher yields of polyelectrolyte, or improvements in technology to prepare polyelectrolytes for use in mining processes are two areas for development. Considerable research effort, however, is necessary.

7. CONCLUSIONS AND RECOMMENDATIONS

We have completed a critical assessment of the literature pertaining to the application of bioadsorption in the mining industry. We regard several types of processes as potential candidates for development at pilot scale. However, hypothetical flowsheets for the generalized process types have indicated unit operations in each process schematic for which current data are inadequate for the immediate design of a pilot-scale system. This lack of data is more significant in some cases than in others. A relative overview of the "state-of-the-art" on bioadsorption processes for heavy metals is presented in Table II.

Bioadsorption of heavy metals by microbial biomass is influenced by many factors including the organism involved, the nature of the metal, culture conditions, the age of the culture, the bioadsorption mechanism, the pH and temperature, the metal concentration in solution, other cations and anions, and the presence of organic complexing agents. In a mining operation, the nature of the ore, the chemical composition of secondary process streams and the presence of organic residues (possibly toxic to the cells) from the extraction procedures will all impact on the process operation and design.

A few limitations in the data in the literature are general to all processes and include:

1) Biosorbents have not been evaluated adequately with complex mixtures of anions and cations e.g. actual mineral processing liquids.

2) With the exception of uranium, data on the recovery of heavy metals from the various biosorbents have not been well documented or investigated. This factor will influence whether or not a biosorbent can be regenerated for reuse.

3) The supply or generation of adequate amounts of biomass and the concomitant requirement for nutrients has seldom been considered. This will be of practical importance for most isolated mine sites.

4) There are virtually no published data on process schematics and mass balance calculations.

These factors will all influence significantly the likelihood of bioadsorption processes being developed to the level that they are viewed as economically attractive routes to recover low concentrations of metals in mine process liquids.

Of the process/biosorbent types identified in our review, algae appear to have limited potential in the Canadian mining environment. The economical generation of adequate amounts of algal biomass will be an obvious practical limitation. Although the use of algal biomass as immobilized systems will possibly bypass this limitation, other types of biomass will probably be equally as effective in that form.

The remaining processes are separated into two categories. The first group include those processes applicable to the recovery of uranium. The bioadsorption behaviour of this metal comes closest to meeting the objective of this program. The second group includes promising technologies for the removal of other heavy metals. Based on current information, they require more extensive investigation at the bench level before being ready for pilot-scale studies.

7.1. The Recovery of Uranium.

We propose that uranium should be the target element in the program leading to Milestone II of this program. The selection is influenced strongly by the efficient regeneration procedures noted for this element with several biosorbents.

We recommmend that the program for the design of a pilot-scale process should include the following steps:

1) Selection of a representative process liquid e.g. a uranium-containing solution from a heap or in situ leach process such as that involved in underground pillar recovery. The composition of this process liquid must be determined in detail.

2) Selection of a biosorbent and hence the type of bioadsorption process.

3) Design of the pilot-scale process for recovery of uranium by bioadsorption.

4) Identification of those parameters for which additional laboratory data will be required.

For the purposes of recovering uranium from process liquids (low concentration of element), we propose fungal mycelium as the biosorbent of choice. However, based on available data, we rank the various process types as to their ability to recover uranium as follows:

1. Fungal mycelium
2. Microbial derivatives (immobilized cells)
3. Mixed microbial (activated sludge) cultures
4. Yeasts or defined microbial cultures.
5. Algae

Selected fungal species have been shown to have a high uptake capacity for uranium(VI) in aqueous solutions. The uranium can be recovered efficiently by washing the metal-laden biomass with dilute solutions of carbonate salts e.g. 0.1M sodium carbonate solution. Both of these attributes are desirable for a bioadsorption process. Factors, which will

require more extensive investigation at the laboratory level prior to proceeding to the pilot-scale process, are the adsorption characteristics of the uranium/biomass combination in the presence of high concentrations of mixed cations and anions e.g. as in true process liquids; the physical characteristics and hence the handling properties of the biosorbent; its long-term durability; and methods and economics of production. The last-named factors will depend on the fungal species selected and possibly its availability as a by-product, e.g. of the fermentation industry. The weight of metal recovered per unit cost of biomass will be an important factor and the operating pilot plant will provide much of these necessary data.

Of the other biosorbents for uranium, the microbial derivatives are similar to fungal mycelium. Attempts are made to improve the physical-handling characteristics of the fungal mycelium by immobilizing or stiffening with polymers and any improvement in this characteristic will have obvious benefits.

Bacterial and algal cells immobilized in gel supports have afforded impressive data for the recovery and elution of uranium from dilute aqueous solutions. Intended for use as columns of biosorbent, these materials have attractive features. However, their application to mining processes is expected to be complicated by problems such as the detrimental effects of constituents in liquors on the physical stability of gelatinous support materials. The use of a process design, which will include an upflow fluidized-bed system, could conceivably alleviate the possible problems from slimes present in the process liquids. The cost of immobilization is an added economic limitation.

Activated sludge(AS) should be investigated as a biosorbent for uranium. Studies to-date have been relatively limited in scope. The promising data obtained by Shumate et al. (1980), with a mixed culture of denitrifying bacteria may be indicative of an untapped potential in AS systems in general. However, these authors provided no data on the feasibility of recovering the uranium from the bacterial cells. Attractive aspects of AS systems will be discussed in the next section.

The adsorption of uranium represents a relatively unique situation due to its particular solution chemistry compared with that of other heavy metals. It has enable researchers to overcome the significant hurdle for a bioadsorption process, namely the recovery of the metal and the regeneration of the biomass. This is considered, at present, an essential feature for a practical process and it maximizes the amount of metal that can be recovered by a limited amount of biosorbent. The regeneration of biosorbent remains, however, a serious limitation in the case of bioadsoption processes for other heavy metals.

7.2. Other Heavy Metals

Data obtained from the development of a pilot-scale process for uranium recovery by bioadsorption will have some relevance to other heavy metals. It will, however, depend on the individual biosorbent. Several of the processes/concepts for the recovery of other heavy metals are at a stage in their development that a more extensive laboratory program might soon permit the design of a pilot-scale process. Based on the available data, we rank the various biosorbents for their potential to recover heavy metals (other than uranium) as follows:

1. Defined bacterial cultures
2. Mixed(activated sludge) cultures
3. Microbial derivatives (immobilized cells, polymers)
4. Fungi and algae

The reversal of the ranking compared with the ranking for uranium reflects some concern about the practical feasibility of using algal cells or fungal mycelium as a general biosorbent i.e. how available are these materials? It does not preclude their use as "chelating ion-exchangers" provided that regeneration methods are available. At present, this requirement has not been satisfied.

A key factor in processes for other heavy metals will be the generation or supply of the required amounts of biosorbent. Ideally, the biosorbent should be capable of being produced using relatively unsophisticated culture techniques to match the situation at an isolated mine site. However, provided that the economics of collection and transport are favourable, the biomass could be generated off-site. Nutrients required for growth must also be readily available and/or inexpensive. Regeneration and reuse of biosorbent would obviously alleviate slightly some of these rather stringent limitations.

Based on current data, organisms of the type isolated from AS systems come closest to matching these cultural and nutritional requirements. The order in which we have ranked defined bacterial cultures and undefined (AS) cultures, is based on the premise that the former system would be targeted at the specific isolation of organisms with both a high rate of biomass production and a high metal uptake capacity. The AS system would involve the natural selection under the prevailing operating conditions, of those organisms with the correct characeteristics to achieve the desired goal.

At present, the data are inadequate to assess accurately the economics of a single-stage process i.e. assuming that the biomass cannnot be regenerated. A two-stage system allowing for reuse of the biosorbent would, however, be the preferred one. Performance data are also needed for both AS systems and defined bacterial cultures applied to mixed composition and complex mine process liquids.

A key factor for the success of the technology will be the development of biomass which can be regenerated and reused. Microbial derivatives are directed at this goal but to be effective, these derivatives must be able to compete against synthetic chemical ion-exchange resins from both the technical and economic standpoint. At present, this, with the exception of uranium, has not been demonstrated in the literature. The concept, however, has long-term potential and future developments should be watched with interest.

In the meantime, an aspect of this technology, which should receive urgent attention, is the search for efficient, inexpensive methods to regenerate the currently more feasible biosorbents e.g. activated sludge and defined microbial biomass.

The heavy metal selected for study will come from the group mercury, copper, lead, cobalt and cadmium. This selection will be an important decision since it will influence the eventual choice of both a mineral processing liquid and the preferred biosorbent. The order that the metals are listed above is a ranking of the metals relative to apparent adsorption efficiencies with different biosorbents. However, other factors must also be borne in mind. For example, mercury shows a very high adsorption by isolated activated sludge biomass but actively growing sludge systems may, however, convert the mercury to volatile compounds. The selection of one metal as being top priority for the mining industry will limit the biosorbents which can be expected to be effective. The selection of a bioadsorption process design will also change the order of ranking of the metals. In a mine process liquor, several heavy metals will be present at varying concentrations. None of the biosorbents demonstrate high specificity and, as noted previously, interelement interferences could be significant.

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TABLE I

UNIT OPERATIONS IN A GENERAL SCHEMATIC FOR BIOADSORPTION

	UNIT OPERATION	SPECIFICATION
1.	Production of Biomass	Off-site vs. on-site Defined culture vs. mixed system Nutrient supply pH Temperature Reactor Design
2.	Isolation of Biomass	Type of organism Filtration characteristics Dewatering
3.	Pretreatment of Biomass	Chemical deactivation Heat deactivation (drying) Immobilization of cells
4.	Adjustment of Feed Solution	pH Chemical composition Filtration (Remove fines)
5.	Bioadsorption Process	Growing culture vs. inactivated cells. Adsorption kinetics Adsorption mechanism Multistage reactor Fluidized bed vs. plugged flow reactor. pH Temperature Competing anions and cations.
6.	Recovery of Metal-laden Biosorbent.	Type of adsorbent Filtration characteristics Dewatering Drying
7.	Recovery of Metal(s)	Leachant Temperature pH Ionic strength Chemical dissolution Incineration Chemical precipitation of digested concentrates

8. Regeneration of Biosorbent	Mechanism of adsorption of metal. (bioadsorption vs. bioaccumulation) Physical durability of adsorbent e.g. resistance to lysis.
9. Treatment and Disposal of Wastes	Effluents from biomass production Chemical effluents Spent biosorbents.

TABLE II

RELATIVE ASSESSMENT OF THE "STATE-OF-THE-ART ON BIOADSORPTION PROCESSES FOR HEAVY METALS

CRITERION	BIOSORBENT / PROCESS				
	ACTIVATED SLUDGE	DEFINED MICROBIAL CULTURE	FUNGAL MYCELIUM	ALGAE	MICROBIAL DERIVATIVES
1. SELECTIVITY FOR INDIVIDUAL METALS	Hg, Cu, Cd, Co Fe, Ni, U, Ra	Cu, Pb, Cd, Hg, Co	U, Th, Pb, Cu.	U, Cu, Cd, Ni Cr, Zn, Co.	U, Th, As, Hg
2. EASE OF SCALE-UP	RELATIVELY EASY	RELATIVELY EASY	DIFFICULT	VERY DIFFICULT	DIFFICULT
3. ADSORPTION CAPACITY AND EFFICIENCY	WILL VARY WITH METAL, METAL CONCENTRATION AND ORIGIN OF THE BIOSORBENT (SPECIES, STRAIN, ETC).				
	1-30% DRY WT. 30-95% UPTAKE	1-30% DRY WT. 30-95% UPTAKE	1-20% DRY WT. 30-95% UPTAKE	1-20% DRY WT. 30-95% UPTAKE	AS HIGH AS 40-50% DRY WT.
4. PREDOMINANT UPTAKE MECHANISM	BIOADSORPTION (BY SELECTION OF CULTURE)	BIOADSORPTION (SELECTED SPECIES)	BIOADSORPTION	BIOACCUMULATION BIOADSORPTION	BIOADSORPTION
5. CAN METAL BE DESORBED EASILY ?	ACID DIGESTION	ACID DIGESTION	URANIUM } - YES THORIUM } OTHER METALS - ?	URANIUM - YES OTHER METALS - ?	URANIUM - YES OTHER } - SOME METALS }
6. REUSE OF BIOMASS	AT PRESENT NO	AT PRESENT NO	URANIUM - YES THORIUM - YES	URANIUM - YES	URANIUM - YES
7. DEGREE OF SIMILARITY BETWEEN TEST SOLUTIONS AND MINE PROCESS LIQUIDS	POOR	GENERALLY POOR	POOR	POOR	POOR
8. SENSITIVITY OF ADSORPTION TO INTERFERENCE (CATIONS, ANIONS, ORGANICS)	AVERAGE	AVERAGE	AVERAGE/HIGH	AVERAGE/HIGH	AVERAGE/HIGH
9. EASE OF GENERATION OF BIOMASS SUPPLY	EASY	EASY	MORE DIFFICULT	VERY DIFFICULT	DIFFICULT
10. CULTURE REQUIREMENTS	SIMPLE - pH - TEMPERATURE - NUTRIENTS	SIMPLE - pH - TEMPERATURE - NUTRIENTS	COMPLEX - pH - NUTRIENTS - TEMPERATURE	MORE COMPLEX - pH - TEMPERATURE - NUTRIENTS - LIGHT	COMPLEX - pH - NUTRIENTS - TEMPERATURE
11. POTENTIAL COSTS OF NUTRIENTS	LOW	LOW	HIGH (POSSIBLE)	HIGH	HIGH (POSSIBLE)
12. USE OF WASTE TREATMENT EQUIPMENT COMMERCIALLY AVAILABLE	FEASIBLE	FEASIBLE	?	NO	?
13. MOST PROBABLE MAJOR ECONOMIC HURDLES	1. NUTRIENT COSTS 2. SINGLE USE OF BIOMASS	1. NUTRIENT COSTS 2. SINGLE USE OF BIOMASS	AVAILABILITY OF BIOMASS AND COST OF PRODUCTION. (NUTRIENT COST, GROWTH RATE)	CULTURE COSTS ENERGY REQUIREMENTS	CULTURE COSTS ISOLATION AND DERIVATIZATION COSTS
14. MOST PROBABLE MAJOR TECHNICAL PROBLEM	BIOMASS HANDLING - PHYSICAL CHARACTERISTICS				
15. MOST PROBABLE TARGET ELEMENTS	Hg=Cu=Pb>Co=Cd	Cu>Cd>Co	U>Th>Pb	U>Cu>C> Ph.	U

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APPENDIX I

COMPUTER LITERATURE SEARCH

APPENDIX I

COMPUTER LITERATURE SEARCH

a) Files Searched

The following files were searched:

Scisearch	-	1974 - 83
Biosis	-	1969 - 83
Life Sciences	-	1978 - 83
Zoological Records	-	1978 - 83
Enviroline	-	1971 - 83
Pollution Abstracts	-	1970 - 83
Environment Bibliography	-	1974 - 83
Aqualine	-	1969 - 83
Compendex	-	1970 - 83
Engineering Meetings	-	1983
NTIS	-	1964 - 83
Metadex	-	1966 - 83

Key authors (those identified in the Request for Proposal and some others) were search in:

Claims U.S. Patents	1970 - 83
World Patent Index	1970 - 83

b) The major keywords used were:

Bioadsorption
Biosorption
Metals
Heavy Metals
Radionuclides

Polysaccharides (extracellular)
Polymers
Alga(e)
Bacteria
Fungi
Mycelium
Bioaccumulation
Microorganisms
Biogeochemistry

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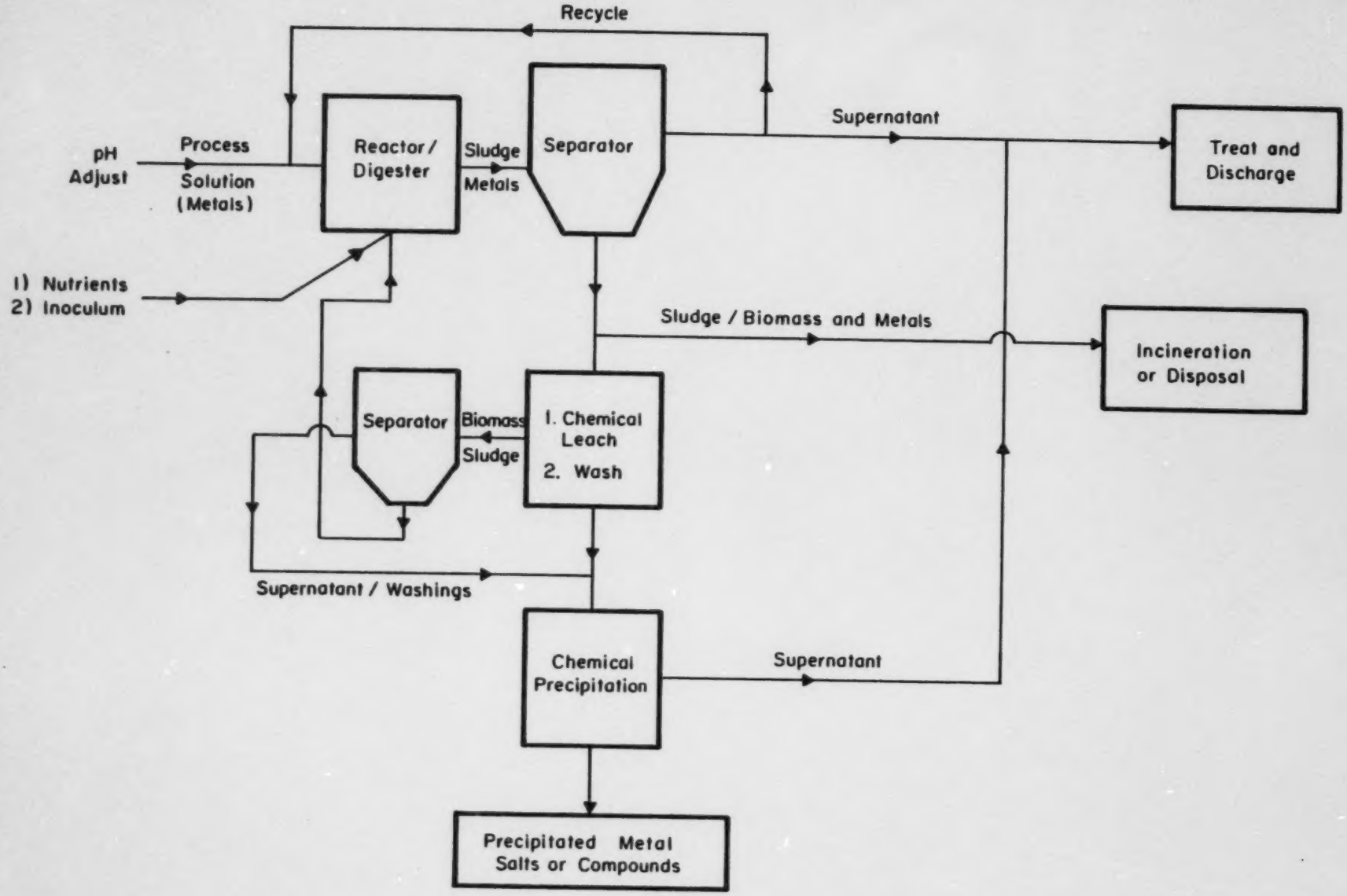
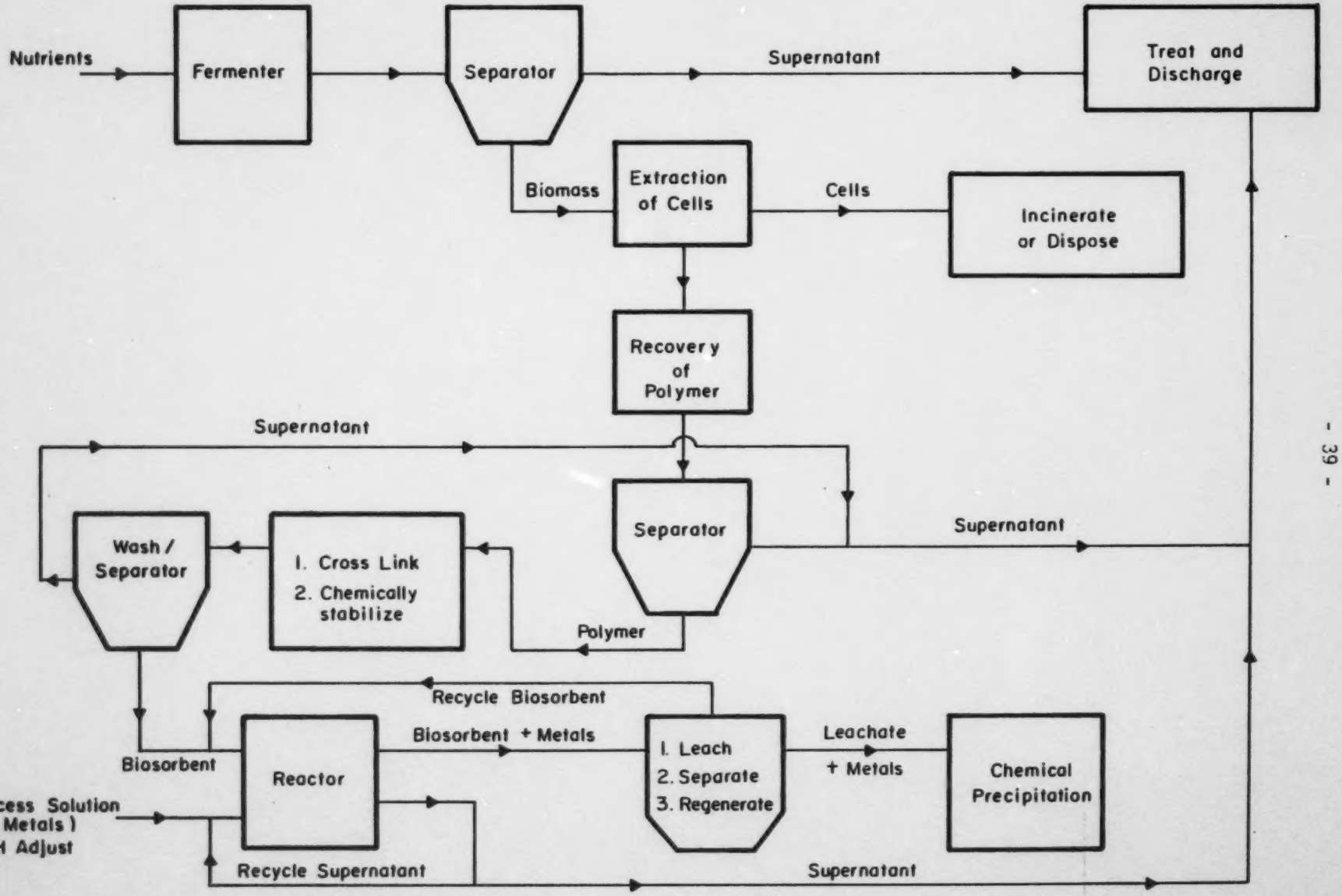
APPENDIX II

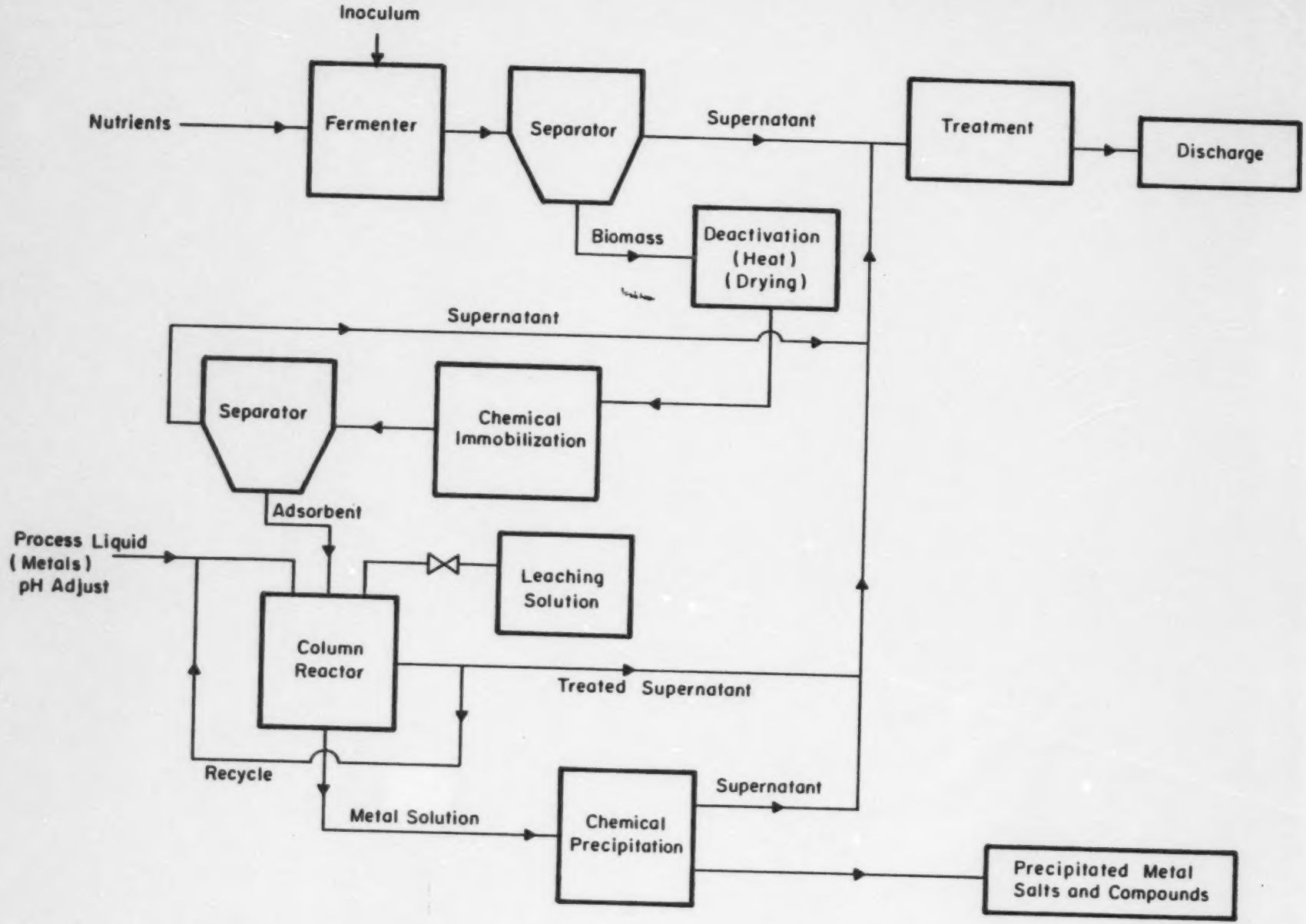
PROCESS SCHEMATIC



MODEL I. SCHEMATIC - ACTIVATED SLUDGE / DEFINED BACTERIAL CULTURE (SINGLE STAGE)



MODEL 2 SCHEMATIC - BACTERIAL POLYMERS



MODEL 3 SCHEMATIC – IMMOBILIZED CELLS

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APPENDIX III

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REPORT TO MILESTONE II
PILOT PLANT SCHEMATIC FOR ADSORPTION OF URANIUM

Allelix Inc.

BIOADSORPTION OF HEAVY METALS FROM MINERAL PROCESSING STREAMS

PHASE I

REPORT TO MILESTONE II

PILOT PLANT SCHEMATIC FOR ADSORPTION OF URANIUM

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BIOADSORPTION OF HEAVY METALS FROM MINERAL PROCESSING STREAMS

PHASE I

REPORT TO MILESTONE II

PILOT PLANT SCHEMATIC FOR ADSORPTION OF URANIUM

1. INTRODUCTION

This report is submitted in accordance with the terms of DSS File No. 26SQ.23440-3-9139.

In our report to Milestone I, it was recommended that the adsorption of uranium by fungal biomass would be the most suitable process around which to design a pilot-scale process for the recovery of heavy metals from mineral processing streams.

In this segment of the Phase I program, process schematics will be proposed to illustrate the transfer of bench-scale technology to a pilot-scale operation.

2. SELECTION OF BIOSORBENT AND FEED SOLUTIONS

2.1. Selection of Biosorbent

The fungal species, Rhizopus or Penicillium, will be used in the proposed pilot process. However, the process design will not be restricted to those species and will have the flexibility to incorporate other fungal biosorbents into the process schematic as they become available.

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2.2. Feed Solution

The chosen feed solution for the process will be the uranium-containing leach liquor from the underground microbial leaching process at Denison Mines, Elliot Lake, Ontario. Data on the typical composition of this leach liquor has been used to select arbitrarily the daily scale of operation for a pilot system. Initial pilot-scale studies would be undertaken with a synthetic liquor similar in composition to the Denison solution.

3. FLOWSHEET DEVELOPMENT

3.1. Selection of Key Process Concepts

Fungal mycelium was recommended for further study because of its meeting one key criterion namely that the adsorbed uranium can be readily desorbed with dilute solutions of alkali carbonates. The typical characteristics of fungal mycelium has influenced our proposal for the type of contactor to be used. A downflow column mode of operation would not appear suitable due to the high probability of plugging. The biosorbent will have too low a density and be too slow settling to permit upflow column operation. The density of the biomass may be increased by attaching, or growing, the organisms onto heavier particles. The biosorbent, however, is not expected to be stable under the elution conditions, so its attachment to inert particles is not likely to be secure.

Biosorbent, which has been stiffened with a suitable polymer might permit the use of resin ion exchange equipment, but the development of biomass with improved physical handling characteristics is considered beyond the scope of this assignment.

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A conceptual biosorbent flowsheet is shown in Figure 1. A filter press is proposed for use as the contacting device. This option (Figures 2 and 3) involves holding the biosorbent in the chamber of three presses, with the solution after contacting the biosorbent following the flow passage for filtrate. The system would operate similar to a three-column, fixed-bed, ion-exchange unit with the loaded biomass eluted in-place and removed only when its replacement is required. It has been assumed that an admixture of filter aid will be necessary to increase permeability. A water flush after both the sorption and desorption cycles will prevent the generation of carbon dioxide in the biosorbent-filled chamber due to acidic leach liquor contacting carbonate residues. Otherwise, channelling and deterioration of adsorption characteristics may be expected to occur due to the presence of gas bubbles.

Based on a feed rate of 4 L/minute, the equipment required for the filter press option has been estimated. The exchange capacity, flow rates, elution efficiency, etc.have been assumed, where necessary, and must be confirmed at bench scale before the equipment can be properly sized.

Several yellow cake precipitation methods are available. Acidification to destroy the carbonate followed by precipitation with ammonia was tentatively chosen. The selection of a preferred method will depend on how the yellow cake would be introduced into an existing plant circuit.

Alternative contacting devices such as stirred tanks (including Cannon mixers) and continuous filters (e.g. drum filter, string discharge) might also be considered. Figure 4 would then be the flowsheet.

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3.2. Design Criteria

The criteria selected for the designing of a process schematic are listed in the Appendix.

3.3. Pilot Plant Operation

The pilot plant will be operated on a synthetic solution and the effect of variables such as flow rate, required concentration of eluant, biomass type, product purity, etc., will be investigated. A final verification of the operating data will be made with an actual sample of a mine solution, such as the Denison underground leach solution. In order to reduce the volume of plant solution required, a number of frames would be removed from the filter presses.

The barren liquor obtained from synthetic solution would be made up to strength with recovered uranium and recycled to feed. Barren liquor from plant leach liquor would be neutralized with lime and assessed for quality, relative to municipal waste discharge standards, before being discarded.

The equipment would require decontamination as part of the clean-up at the termination of the program.

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4. RECOMMENDATIONS

1) A pilot plant following one of the suggested flowsheets should be designed and constructed. Back-up bench scale work should be performed to confirm the respective uranium sorption and stripping isotherms and rates, as well as the flow properties of the chosen biomass.

2) The candidate biomass should be subjected to testing in the pilot plant up to 50 cycles using a synthetic uranium-containing solution. Loss of biomass, degradation of transfer and flow properties will be followed.

3) Testing on synthetic solution should be followed by trials using a typical plant isolate.

4) A second candidate biomass should be investigated and tested.

5) An engineering company should be involved throughout the pilot plant test work to observe and obtain preliminary design data for the construction of an on-site operation.

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FIGURES

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FIGURE 1

U_3O_8 BIOSORPTION

CONCEPTUAL FLOWSHEET

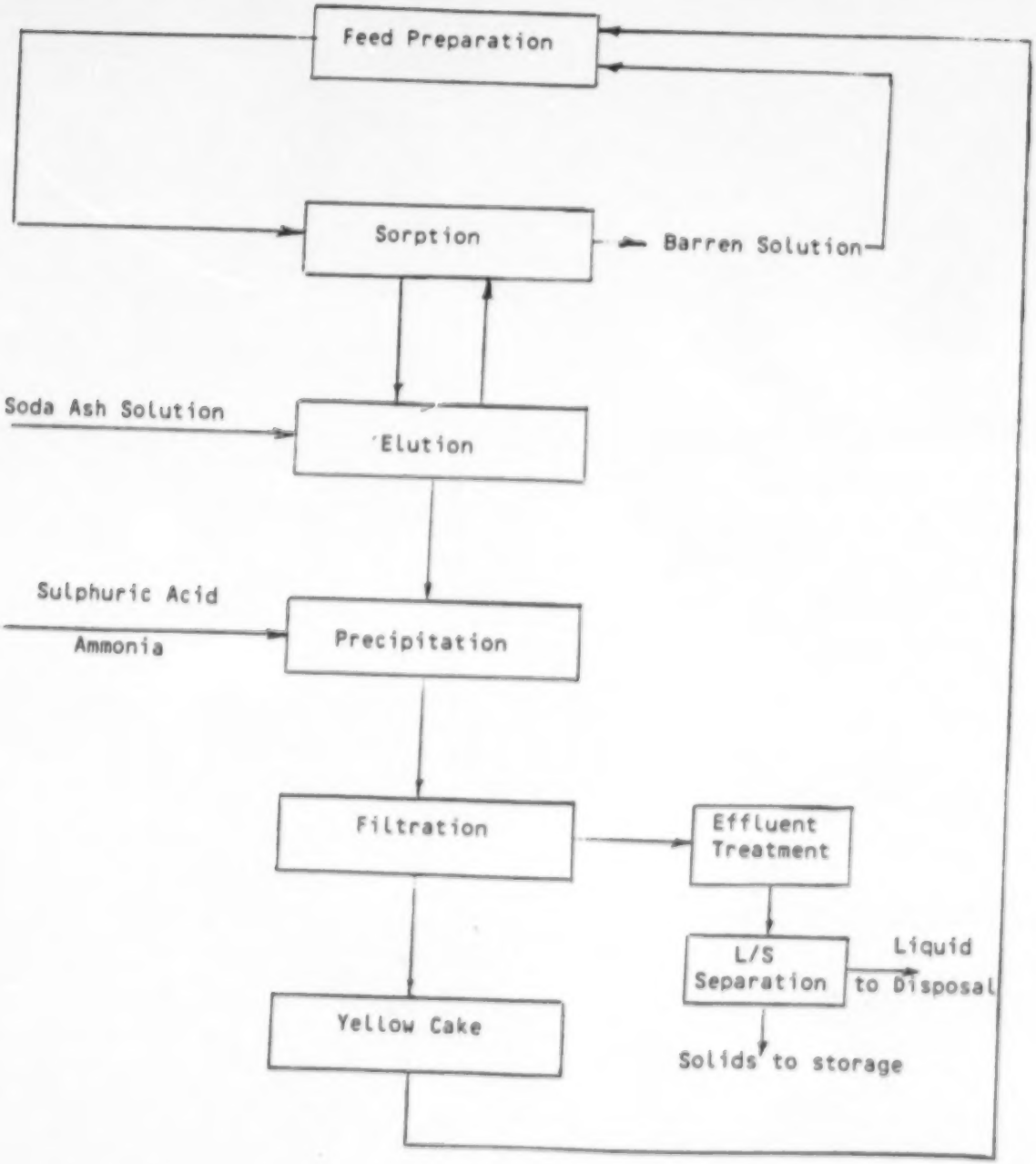

FIGURE 2

U_3O_8 BIOSORPTION

FILTER PRESS OPTION

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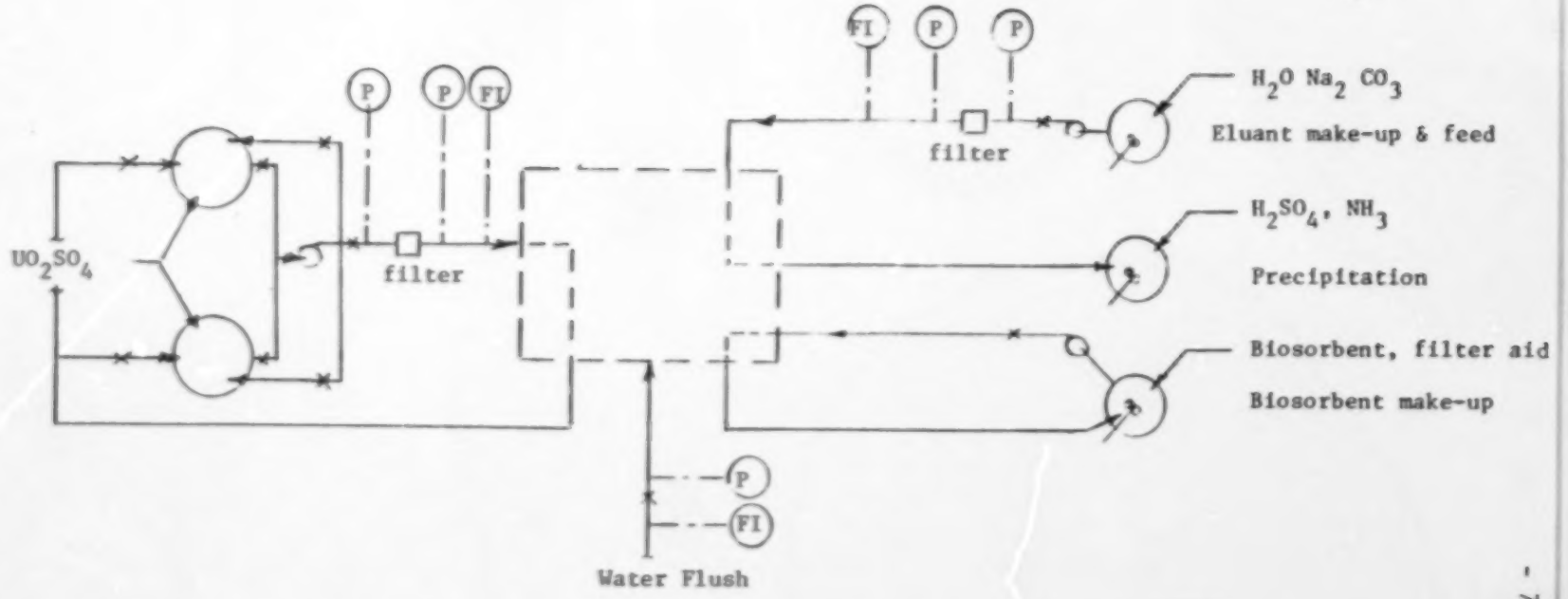

Feed Tanks

Biosorbent System

Eluant, Precipitation Biosorbent Tanks

FIGURE 3

U_3O_8 BIOSORPTION

THREE UNIT SORPTION SYSTEM

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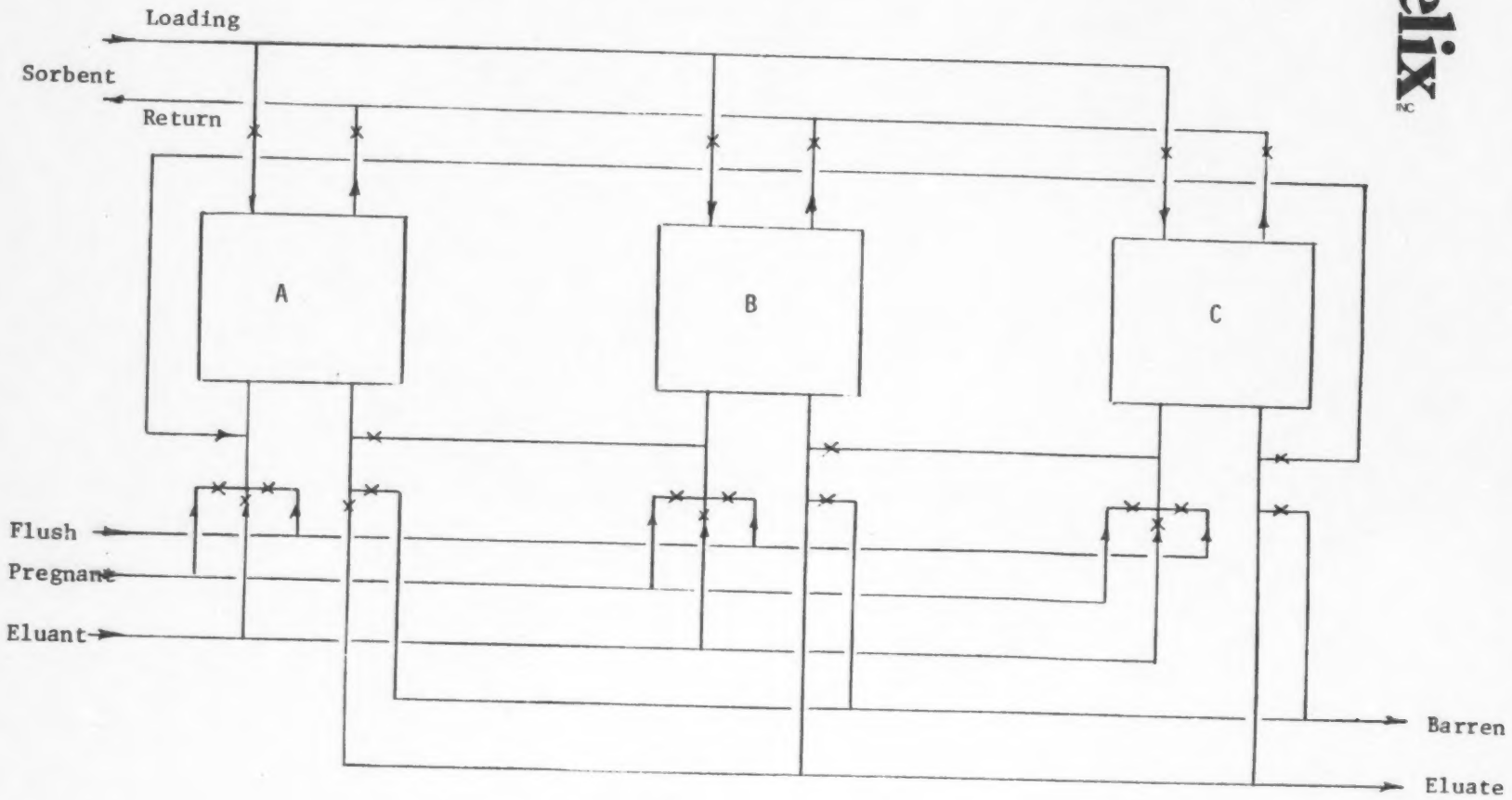

A,B,C: Filter press loaded with biosorbent

FIGURE 4

U_3O_8 BIOSORPTION

DRUM FILTER OPTION

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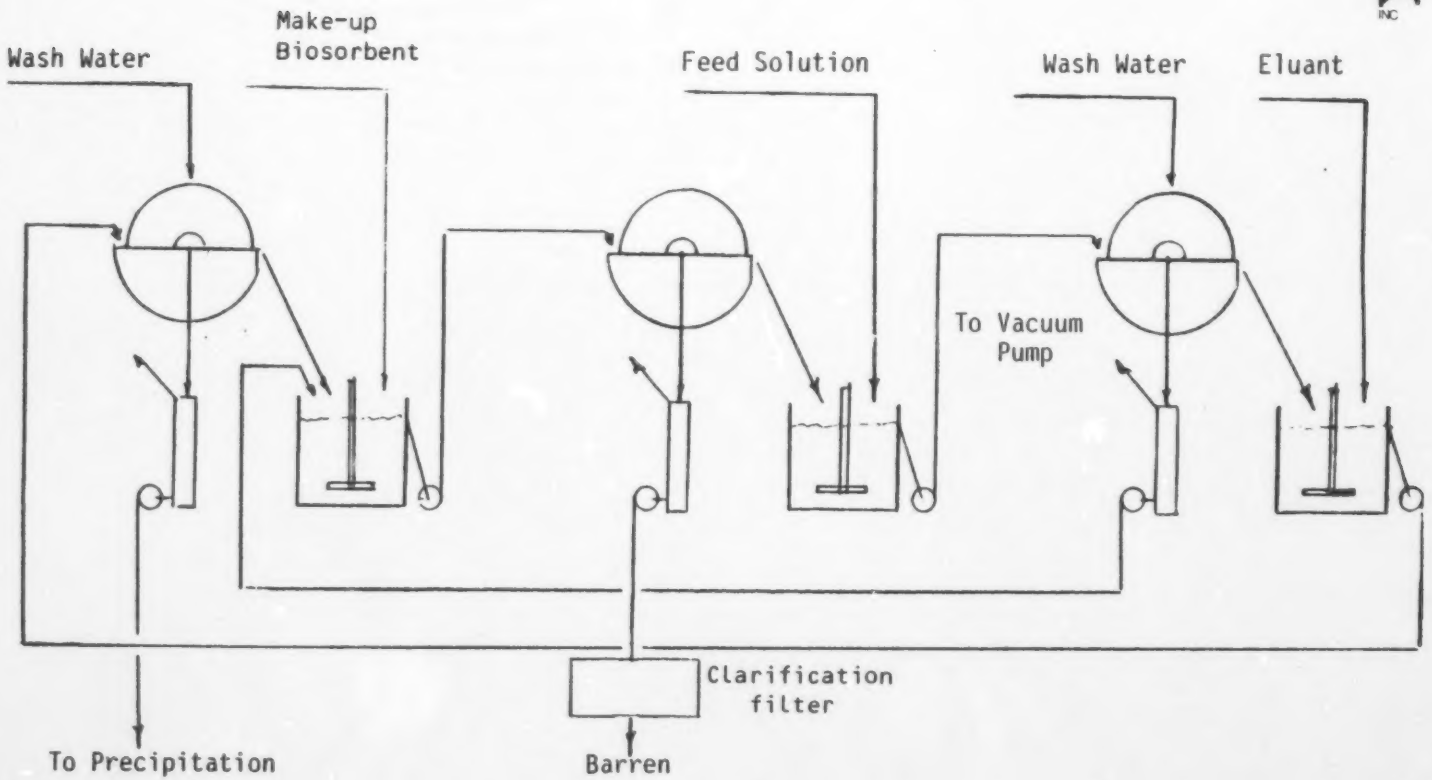

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APPENDIX

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APPENDIX

DESIGN CRITERIA

Feed Solution

Flow Rate	-	4.0 L/min
Uranium Concentration	-	0.1g/L
Ferrous Ion Concentration	-	0.2g/L
Ferric Ion Concentration	-	0.6g/L
pH	-	2.0

Feed System

Tanks

Number	-	2
Capacity, each	-	$2.4M^3$
Material of construction	-	Acid Resistant

Contactors

Number	-	3
Type	-	Plate and Frame Press
Flow area, each contactor	-	$0.66M^2$
Active volume	-	16L approx.
Material of construction	-	Acid Resistant
Arrangement: absorption	-	Two in series
elution	-	One

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Absorption Cycle

Operation	Flow Rate L/Min	Time Hours	Total Flow L
Absorption to barren	4.0	8	1920
Flush to barren	1.0	0.5	30
Eluant to pregnant	1.0	0.2	12
to precipitation	1.0	0.3	18
Flush to precipitation	1.0	0.2	12
to pregnant	1.0	0.3	18

Eluant

- Tank capacity - 75 L
- Volume per cycle - 30 L
- Sodium carbonate - 0.1 M
- Agitation - mild

Precipitation

- Tank capacity - 75 L
- Volume per cycle - 30 L
- Material - acid resistant
- Agitation - mild
- U_3O_8 per cycle - 192 grams
- H_2SO_4 per cycle - 350 grams
- NH_3 per cycle - 40 grams

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Biosorbent Make-up

Tank capacity	- 52 L
Biosorbent/batch	- 1.3 kg dry weight
Filter aid/batch	- 4.0 kg
Agitation	- to suspended filter aid

Notes:

1. Feed tanks are sized to hold the contents of a day's operation. They should be designed to empty completely (e.g. shallow cone bottom).

2. Solids must not be allowed to accumulate in the contactor distribution system; filters are required on the feed and eluant solutions. Cartridge type are suggested.

3. The yellow cake recovered in precipitation will be filtered, washed, redisolved in sulphuric acid, and returned to the feed tank.

The amount of yellow cake in one batch will be low enough to permit bench scale filtration and handling.